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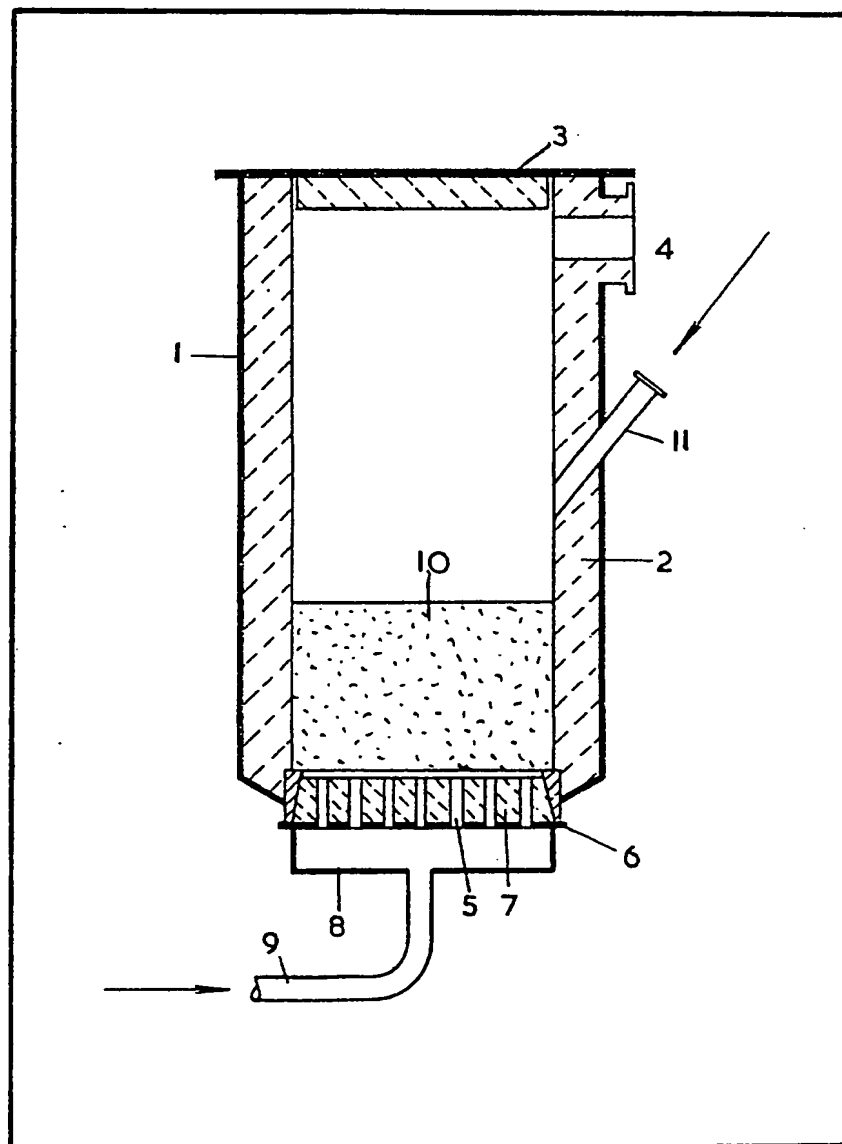
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(54) Refractory lined vessel and method of use

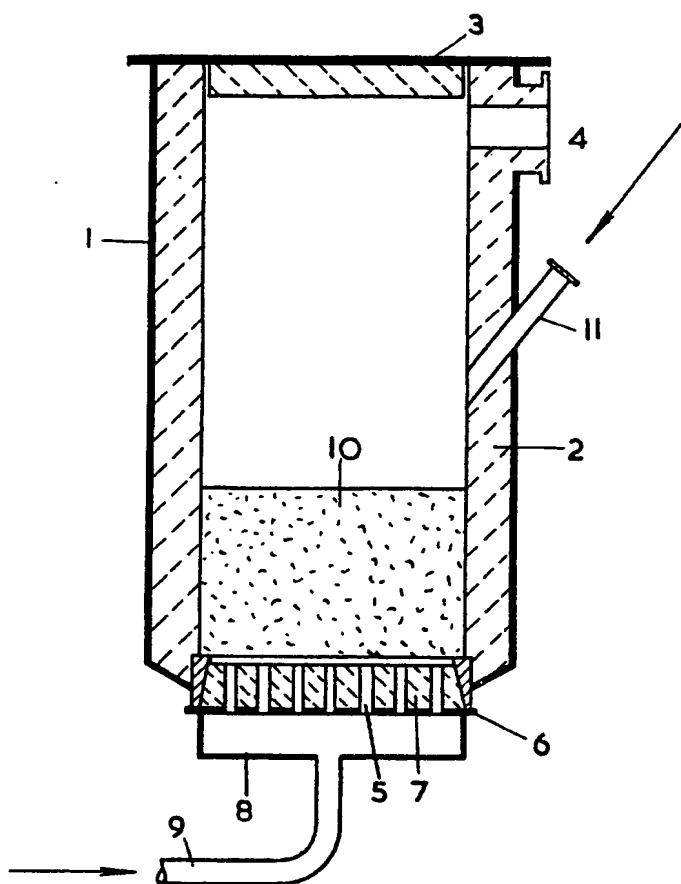
(57) A vessel for use in the chlorination of a titaniferous material having an outer shell-like retaining wall, inlet means for the material and outlet means for discharge of gaseous products with a base provided with a means to introduce a gas into the vessel and the shell-like retaining wall having a refractory lining and the base

an infill material in which the lining, infill material and/or means to introduce a gas are formed of a refractory concrete containing an aggregate and a high alumina binder containing up to 20% by weight of calcium chloride.

The chlorinator vessel has been found to have a much improved life during use with the refractory concrete, the material being capable of withstanding the action of chlorine gas over extended periods.



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SPECIFICATION

Refractory lined vessel and method of use

This invention relates to refractory lined vessel, particularly a chlorinator, and its method of use.

- 5 During use of a chlorinator for chlorination of a titaniferous material existing refractory materials exhibit wear when used as linings and this necessitates expensive repair or replacement at frequent intervals. There is a need for such
- 10 chlorinators having longer lives than at present between repairs.

- According to the present invention a vessel suitable for use in the chlorination of a titaniferous material comprises an outer shell-like retaining wall having a closed upper end and a base, inlet means to introduce a titaniferous material into the vessel and outlet means located at or adjacent the upper end for the discharge of gaseous reaction products, said base having means to introduce a
- 15 gas into the vessel and to distribute said gas over the horizontal cross-sectional area of the vessel, said retaining wall having a refractory lining and said base having refractory infill material between individual means to introduce and to distribute
- 20 said gas and, said individual means, said lining and/or said infill material being formed of a refractory concrete containing an aggregate and a high alumina containing cementitious binder containing up to 20% by weight of added calcium chloride base on the weight of said refractory
- 25 concrete.

- Preferably the cementitious binder contains aluminium values in an amount of at least 50% by weight when expressed as Al_2O_3 and most
- 35 preferably contains aluminium values in an amount of at least 65% of weight when expressed as Al_2O_3 of the weight of the binder. The remainder of the composition of the binder will usually be constituted by a majority percentage
- 40 by weight of calcium values and minor amounts of silica values and iron values together with other elemental values in trace quantities. Depending on the particular amount of aluminium values the amount of calcium values will be from 25% to
- 45 40% by weight when expressed as CaO of the weight of the binder.

- Overall it is desired that the particular concrete-formed on mixing the aggregate and binder usually will have a composition so that it contains
- 50 aluminium values in an amount of 44% to 50% by weight expressed as Al_2O_3 , silicon values in an amount of from 40% to 45% by weight when expressed as SiO_2 , iron values in an amount of not more than 2% by weight when expressed as
- 55 Fe_2O_3 and calcium values in an amount of from 4% to 7% by weight when expressed as CaO.

- The addition of calcium chloride to the mixture of aggregate and binder has been found to increase the life of refractory concrete by a
- 60 surprising extent. This is most surprising particularly when considering the destructive atmosphere present in a chlorinator with the presence of chlorine gas, acid reaction products together with some inevitable oxychlorides. A

- 65 simple addition of calcium chloride would hitherto hardly have been considered to be of value. Nevertheless this addition is of considerable significance. The amount of added calcium chloride is up to 20% by weight of the refractory concrete dry mixture and preferably is from 1.5% to 10% by weight.

- The chloride can be added in the dry form to the other ingredients or alternatively the chloride can be added as a solution in the water required to effect setting of the refractory concrete.

- The proportion of aggregate to binder is chosen to produce the required composition of the final concrete but usually depending on the particular composition of the ingredients from 2.5
- 80 to 5 parts by weight of aggregate will be mixed with one part by weight of the binder. The most preferred proportion of aggregate to binder is 3 parts by weight of aggregate to one part by weight of binder.

- The aggregate can have a wide range of particle size but usually will have a particle size range of 8 mm to dust. A typical useful aggregate is a fired flint clay of the desired size.

- Sufficient water is added to the dry mixture to give the required consistency and to be sufficient to permit complete setting of the refractory concrete to take place. The mixture can be applied by casting, gunning, trowelling or by extrusion as is appropriate.

- The vessel is of particular use in the chlorination of a titaniferous material to produce titanium tetrachloride. The chlorination is carried out in the presence of a carbonaceous reducing agent, e.g. coke, by chlorine gas passing upwardly through a bed of the reactants at such a rate and density as to maintain the bed in fluid suspension. Normally the bed of material is heated to at least 800°C to initiate the chlorination reaction.

- The bed of titaniferous material, which most suitably is ilmenite or more preferably mineral rutile, is retained within the chlorinator on the base formed by an array of gas distribution tubes or tuyeres carried by a lower support plate. Refractory infilling material is provided between the gas distribution tubes. The gas distribution tubes or tuyeres can be formed of a refractory material similar to that used to form the lining. Normally a wind box or gas distribution chest is located below the array of gas distribution tubes so that as to fluidise the bed and to effect the chlorination reaction can be fed to the tubes from a suitably located inlet.

- One form of chlorinator constructed in accordance with the invention will now be described by way of example only with reference to the attached drawing which is a diagrammatic section of a suitable vessel.

- The chlorinator consists of an outer shell 1 having a refractory lining 2. The upper end of the shell 1 is closed by a lined lid 3 and the shell 1 has an upper outlet 4 for chlorination products. Across the base of the shell 1 is positioned an array or an assembly of gas distribution tubes 5 carried on a support plate 6 with the spaces between

adjacent tubes 5 being filled by refractory infill 7 similar to that forming the lining 2. Below the support plate 6 is a wind box or gas distribution chest 8 having an inlet 9 for a gas.

- 5 In use the bed 10 of the titaniferous material to be chlorinated is carried by the array of tubes 5 and an inlet port 11 if provided through which the bed may be replenished in use.

- The invention also includes a method of
10 chlorination of a titaniferous material to produce titanium tetrachloride which comprises establishing a bed of a titaniferous material to be chlorinated and a reducing agent on the base of a vessel in accordance with the invention and
15 heating the bed to the desired reaction temperature and passing chlorine gas through the gas distribution tubes to react with the titaniferous material and to maintain the bed in fluid suspension and collecting the titanium
20 tetrachloride produced by the chlorination.

The invention is additionally illustrated in the following Example.

Example

- A chlorinator vessel having a base with an infill
25 which had been cast from a concrete mixture containing a prefired flint clay aggregate and cementitious binder containing a source of alumina in an amount of 7.1% by weight expressed as Al_2O_3 on weight of binder, iron
30 oxide in an amount of 0.25% by weight and a source of calcium in an amount of 27% by weight expressed as CaO was assembled. Calcium chloride was mixed with the water for setting and added to the dry mixture. The amount of calcium
35 chloride was 2.5% by weight of the dry mixture. A bed comprising a mixture of coke and mineral rutile was formed on the base and heated to the temperature of chlorination. Chlorine gas was then passed through the bed for a period of 1200
40 hours during which time further supplies of the bed material was added and the chlorination products continuously withdrawn through an upper part of the vessel.

- After 50 days continuous operation
45 chlorination was ceased and the interior of the vessel examined after it had been allowed to cool.

- Close examination of the base indicated that little or no erosion had taken place of the surface of the lining and in fact the tuyeres which had been cast from a conventional type of concrete mixture had eroded to leave the lining standing proud of the upper surface.

- A similar infill material without added $CaCl_2$ when used for a similar period had worn to such
55 an extent that the tuyeres themselves stood proud of the surface of the infill.

It was estimated that the life of the infill containing $CaCl_2$ was at least twice that of an infill free of added $CaCl_2$.

60 Claims

1. A vessel suitable for use in the chlorination of titaniferous material which comprises an outer shell-like retaining wall having a

- closed upper end and a base, inlet means to
65 introduce a titaniferous material into the vessel and outlet means located at or adjacent to the upper end for the discharge of gaseous reaction products, said base having means to introduce a gas into the vessel and to distribute said gas over
70 the horizontal cross-sectional area of the vessel, said retaining wall having a refractory lining and said base having refractory infill material between individual means to introduce and to distribute
75 said gas and, said individual means, said lining and/or said infill material being formed of a refractory concrete containing aggregates and a high alumina containing cementitious binder having up to 20% by weight added calcium
80 chloride based on the weight of said refractory concrete.

2. A vessel according to claim 1 in which the cementitious binder contains aluminium values in an amount of at least 50% by weight expressed as Al_2O_3 of the weight of the binder.

- 85 3. A vessel according to claim 1 or 2 in which the cementitious binder contains aluminium values in an amount of at least 65% by weight expressed as Al_2O_3 of the weight of the binder.

4. A vessel according to any one of the
90 preceding claims in which the amount of calcium values is from 25% to 40% by weight expressed as CaO of the weight of the binder

5. A vessel according to any one of the preceding claims in which the particular concrete forming said lining and/or said infill contains
95 aluminium values in an amount of from 44% to 50% by weight expressed as Al_2O_3 , silicon values in an amount of from 40 to 45% by weight expressed as SiO_2 , iron values in an amount of not more than 2% by weight when expressed as
100 Fe_2O_3 and calcium values in an amount of from 4% to 7% by weight when expressed as CaO

6. A vessel according to any one of the preceding claims in which the amount of calcium
105 chloride is from 1.5% to 10% by weight on the weight of refractory concrete dry mixture.

7. A vessel according to any one of the preceding claims in which the amount of aggregate is from 2.5 to 5 parts by weight per 1
110 part by weight of binder.

8. A vessel according to claim 7 in which the amount of aggregate is 3 parts by weight to 1 part by weight of the binder.

9. A vessel according to any one of the preceding claims in which the aggregate has a
115 particle size of 8 mm to dust.

10. A vessel according to any one of the preceding claims in which the aggregate is a fired flint clay.

- 120 11. A method of chlorination of titaniferous material which comprises establishing a bed of titaniferous material to be chlorinated and a reducing agent on the base of a vessel constructed in accordance with any one of the preceding claims and heating the bed to the
125 desired reaction temperature and passing chlorine gas through the gas distribution tubes to react with the titaniferous material and to maintain the

bed in fluid suspension and collecting the titanium tetrachloride thus produced by the chlorination process.

12. A method according to claim 11 in which
5 the bed of titaniferous material is heated to at

least 800°C to initiate the chlorination reaction.

13. A vessel suitable for use in the chlorination of a titaniferous material constructed and arranged substantially as described herein and
10 shown in the accompanying drawing.